

TITLE OF THE INVENTION
SEMICONDUCTOR DEVICE AND METHOD FOR MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

5 The present invention relates to a semiconductor device,
and in particular to a semiconductor device utilizing
quantum effect.

10 A semiconductor device having a quantum microstructure
such as quantum well, quantum wire, quantum box, etc. is
preferably used as a semiconductor light emitting device,
and it exhibits excellent characteristics such as low
threshold current, high modulation band, high coherence
characteristics, etc. through quantum effect of electrons
and holes. Further, such effects are remarkably noted in
15 case distortion lower than critical film thickness is
introduced to an active layer.

20 The methods to prepare quantum wires are as follows: a
method to prepare quantum well structure and to obtain
quantum wires by combining fine photolithography using
electron beam exposure with vertical etching using ion
beam, and a method to provide a V-shaped groove on a
substrate as shown in Fig. 8 and to grow double hetero
structure over the entire substrate surface having a groove
with V-shaped cross-section (hereinafter referred as "V-
25 groove").

 However, the former method is disadvantageous in that
side walls of the groove may be extensively damaged during
fabrication and the quantum wires are often in poor quality.

097848-02001

On the other hand, the latter method has advantages in that quantum wires can be selectively prepared by utilizing dependency of the growing speed on orientation, while it has drawbacks in that the bottom of the formed V-groove may be rounded depending upon the composition of the portion to form the V-groove, or oxide film is formed on the etching surface or contamination is caused by impurities during wet etching, or the bottom of V-groove is rounded due to etching.

Because quantum wire is a minute area, optical density on the light outgoing side tends to increase extremely when applied on laser structure, and only very weak light output can be obtained.

In a microstructure such as quantum wire, more quantum effects are present in thick film than in plane, and this is convenient to have high gain. When it is attempted to grow a distortion active layer with lattice mismatch ratio of 1 to 2% where the effect of distortion appears on flat substrate surface, the film thickness, at which dislocation starts to occur, i.e. critical film thickness, is only in the order of 10 to 20 nm because stress is applied on all over the surface of the distortion active layer. Thus, it is often not possible to have thick distortion active layer when it is to be utilized as quantum wire.

For this reason, it is an object of the present invention to provide a structure, in which quantum wires with good quality can be easily obtained, and a method to prepare such a structure.

It is another object of the present invention to

improve efficiency of a semiconductor device.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Fig. 1 is a schematical drawing of longitudinal section of a semiconductor device manufactured in embodiments 1 and 2 of the present invention;

Fig. 2 represents manufacturing processes of a semiconductor device according to the present invention;

10 Fig. 3 represents a schematical drawing of longitudinal cross-section of a semiconductor device manufactured in embodiments 3 and 4 of the present invention;

Fig. 4 represents a schematical drawing of longitudinal cross-section of a semiconductor device manufactured in embodiment 5 of the present invention;

15 Fig. 5 represents a schematical drawing of longitudinal cross-section of a semiconductor device manufactured in embodiment 6 of the present invention;

20 Fig. 6 represents a status of PL light emission at room temperature of a sample prepared in the embodiment 1 of the semiconductor device of the present invention;

Fig. 7 shows a status of PL light emission at room temperature of a sample prepared in the embodiment 3 of the present invention; and

25 Fig. 8 is a schematical drawing of a typical cross-section of an element using a conventional type quantum wire.

SUMMARY OF THE INVENTION

After having elaborately studied, the present inventors

have found that the above problems can be solved by forming a V-groove having V-shaped cross-section on a semiconductor substrate or on an epitaxial growth layer grown on a semiconductor substrate and by providing an active layer only at the bottom of said V-groove.

Specifically, the present invention provides a semiconductor device having a V-groove with V-shaped cross-section on a semiconductor substrate or on an epitaxial growth layer grown on a semiconductor substrate, and an active layer is provided only at the bottom of said V-groove. The invention also provides a semiconductor device, which is manufactured by the steps of forming a stripe-like etching protective film in $\langle 011 \rangle$ direction of a semiconductor substrate or of an epitaxial growth layer, performing gas etching using hydrogen chloride as etching gas on a semiconductor substrate or on an epitaxial growth layer grown on a semiconductor substrate to form a V-groove, and forming an active layer at the bottom of said V-groove. The invention also provides a method for manufacturing said semiconductor device.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following, detailed description will be given on the present invention.

The structure of a semiconductor device according to the present invention can be preferably used for III - V compound semiconductor and II - VI compound semiconductor. The structure according to the present invention is

preferably used as an electronic element utilizing conduction of carriers in an active region, or more preferably, it is used as a light emitting semiconductor device.

5 Description is now given on the structure of the semiconductor device of the present invention, referring to the device in Fig. 1 where the structure is grown on (100) face GaAs substrate of III - V compound prepared in the embodiment.

10 The (100) face is used because symmetry or rectilinearity of quantum well is under influence of symmetry and rectilinearity of V-groove and the most advantageous orientation is selected. A substrate of any orientation may be used unless there is extreme influence of
15 symmetry and rectilinearity of quantum well. Of course, the same applies to off-angle orientation. The V-groove of the present invention is provided on a substrate or on an epitaxial layer grown on a substrate. The direction of the V-groove is preferably deviated by less than 10° from
20 <011> direction, or more preferably by less than 5°. If it is deviated by more than 10° from <110> direction, the sides of the V-groove tend to be in form of notched steps, and this is not very desirable.

25 An active layer 4 is formed on a portion at the bottom of the V-groove. In case a quantum well structure is used as the active layer, the thickness "h" of the active layer 4 is preferably 50 nm or less for the use as quantum wires, or more preferably 20 nm or less. The linewidth "w" of

When the distortion active layer 12 is grown locally as in the present invention, less stress is applied on the distortion active layer 12, and it is possible to obtain the distortion active layer 12 with thick film.

5 As shown in Fig. 4, an optical guiding layer 10 having refractive index lower than that of the active layer but higher than that of the cladding layer may be formed between the active layer 4 and the cladding layer 5 inside the V-groove. In this case, a quantum wire having the
10 better light emitting characteristics can be obtained. By adopting such a structure, light from laser beam generated by recoupling of electrons and holes in the active layer, which comprises the quantum wire, comes out around the quantum wire, and this makes it possible to increase light
15 output.

In the other method to increase light emitting characteristics as shown in Fig. 5, a double hetero structure, which has a first optical guiding layer 13 with higher refractive index sandwiched in vertically between a
20 first cladding layer 3 and a second cladding layer, both layers having lower refractive indices, is grown epitaxially in form of a semiconductor substrate, and a V-groove is formed on the epitaxial growth layer of double hetero structure, whereby the active layer 4 at the bottom
25 of V-groove is in contact with the first optical guiding layer 13 on the side of the V-groove. In this case, too, it is preferable that an optical guiding layer 10 (a second optical guiding layer) is present between the active layer 4

when the active layer is provided in contact with the etching surface.

The method to manufacture a V-groove having V-shaped cross-section, which is one of the features of the semiconductor device of the present invention, is as follows:

The V-groove may be in such a structure that it has no longitudinal length such as inverted pyramid.

If the semiconductor substrate is made of a material, which can be used as a cladding layer, it may be used as it is. Normally, however, a layer to become the cladding layer 3 outside the V-groove is first epitaxially grown on the semiconductor substrate. In this case, it is preferable to use organic metal vapor phase growth method (MOCVD method). The layers to be epitaxially grown include, in addition to the cladding layer 3, a buffer layer 2 provided between the substrate and the cladding layer so that impurities or defects in early stage of growth do not reach the light emitting layer, an optical guiding layer 10 provided on the cladding layer 3 with the purpose of increasing light output, a high resistance cladding layer 9 for confining electric current within the V-groove, and a cap layer 7 for preventing oxidation and protecting the surface.

On this epitaxial wafer surface, a stripe-like etching preventive film is formed using patterning process such as photolithography. As the etching preventive film, any type already known may be used, and it is preferable to use

2

a silicon nitride film 8, a silicon oxide film, etc. In this case, it is preferable that the direction of the stripe of the etching preventive film is in $\langle 110 \rangle$ direction.

5 Thereafter, using the etching preventive film as mask and HCl as etching gas, in-site gas etching of the semiconductor substrate or the epitaxial layer is performed, and a V-groove with sharp edge is formed. Using HCl as the etching gas, the side of the V-groove is turned to a {111} B face 6. Besides HCl, a gas having at least one type of halogen element such as hydrogen bromide, arsenic trichloride, phosphorus trichloride, chlorine, etc. may be used as the etching gas, and it is possible to obtain a V-groove, which has the side as {111} B face as in the case where HCl is used.

10 Etching may be carried out in an independent reaction chamber, but it is preferable that the substrate is placed in a reactor for organic metal vapor phase growth method and the etching gas is introduced in the reactor because the active layer and the cladding layer can be grown continuously without exposing the substrate to the air. By this method, an active layer with good quality can be obtained even when the active layer is directly grown on the etching surface because the impurities do not remain on the etching surface or oxide film is not formed.

20 Further, an active layer is then formed in the V-groove, and MOMBE, CBE, etc. may be applied for this purpose, while it is preferable to use the organic metal vapor phase growth

method. In this case, no crystal growth occurs from the side of the V-groove because the side of the V-groove is a {111} B face. The generated active layer material remains at the bottom of the V-groove, and the active layer is formed only at the bottom.

It is preferable that inclination of the V-groove is on the {111} B face. The {111} B face is defined as a {111} face where only V compounds are aligned on the surface in case of III - V compound semiconductor, and as a {111} face where only VI compounds are aligned on the surface in case of II - VI compound semiconductor. This is because steric hindrance of V atoms occur or $V/III > 1$ on the {111} B face, and crystal growth is mostly unlikely to occur and growth is easily started from the bottom of the V-groove.

Subsequent to the formation of the active layer, a cladding layer is grown on upper portion of the active layer within the V-groove. Also, when necessary, a cap layer for preventing oxidation and protection on the surface of the growth layer within V-groove and a contact layer for decreasing contact resistance during electrode formation may be formed.

In the following, more detailed description will be given on the present invention referring to embodiments, whereas the invention is not limited to these embodiments, and it is needless to say that changes and modifications can be made without deviating from the spirit and the scope of the present invention.

(Example 1)

First, on a (100) GaAs substrate 1, a GaAs buffer layer 1 (0.5 μm), $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ cladding layer 3 (2 μm) and a GaAs cap layer 7 (20 nm) were formed by MOCVD method in this order. On the surface of this epitaxial substrate, silicon nitride film was formed by PCVD method, and the surface was masked by photolithography method and plasma etching method in such manner that the silicon nitride film 8 (SiN_x) of 1 μm in width extending in [011] direction was aligned at every 1 μm (Fig. 2 (a)). This stripe-like SiN_x film is used as a protective mask for gas etching and selective growth. The masked sample was set again to the MOCVD system. After setting, temperature was raised to 700°C under arsine (AsH_3) atmosphere. Then, etching was performed using HCl gas, and a V-groove of 0.7 μm in depth having the {111} B faces 6 on both sides was formed (Fig. 2 (b)). Immediately after the etching was stopped, trimethyl gallium (TMG) was supplied with the temperature maintained at 700°C, and a GaAs quantum wire active layer 4 was formed in the V-groove (Fig. 2 (c)). Further, trimethyl aluminum (TMA) was supplied simultaneously with TMG, and an $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ cladding layer 5 of 0.5 μm was formed. Next, the supply of TMA was stopped and a GaAs cap layer 7 of 10 nm was formed (Fig. 2 (d)). In this case, the {111} B face is selectively formed by gas etching because etching proceeds much slower on this face compared with the other faces. Because epitaxial growth is difficult to perform on the {111} B face, no growth occurs on the side wall of the V-groove. As a result, GaAs

098483260

5

10

15

20

25

quantum wire is self-matchingly formed at the bottom of the V-groove. By supplying HCl at a rate of about 1 sccm, i.e. by the same number of mols as III raw material even during the growth, deposition of AlGaAs polycrystal on the silicon nitride film 8 was prevented. This method to supply HCl during growth is preferably used in case aluminum composition in the GaAlAs layer is 0.4 or more. This enables selective growth of AlGaAs having high aluminum composition, and this is effective for confinement of carriers to the quantum wire active layer 4.

The sample thus grown was examined under scanning electron microscope. Fig. 1 schematically shows how it looked. Under-etching phenomenon with the etching extending under the mask of silicon nitride was not observed, and a V-groove with sharp edge could be formed. Only at the bottom of the V-groove, a GaAs wire of 9 nm in height (h) and 20 nm in lateral width (w) at the tip was buried. When PL (photoluminescence) of this sample was examined, light emission from the quantum wire was conspicuously observed at 77 K and at room temperature (300 K). Fig. 6 shows the data at room temperature. These results suggest quantum wire of high quality and with fewer damage can be easily obtained.

(Example 2)

A sample was prepared by the same procedure as in Example 1 except that the composition of the cladding layer 5 inside the V-groove was $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$, and light emission intensity was examined. Apparently, light emission

growth was difficult to perform on the {111} B face 6, and no growth occurred on the side walls of the V-groove. As a result, a GaAs quantum wire was formed self-matchingly at the bottom of the V-groove. By supplying HCl at a rate of about 1 sccm, i.e. by the same number of mols as that of III raw material even during growth, deposition of AlGaAs polycrystal on the silicon nitride film 8 was prevented. This method to supply HCl during growth is preferably used in case aluminum composition in the GaAlAs layer is 0.4 or more. This enables selective growth of AlGaAs having high aluminum composition, and this is effective for confinement of carriers to the active layer 12.

The sample thus grown was examined under scanning electron microscope. Fig. 3 schematically shows how it looked. Under-etching phenomenon with the etching extending under the mask of silicon nitride did not occur, and a V-groove with sharp edge was formed. Only at the bottom of this V-groove, $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$ wire was buried. In case it was grown on a flat substrate, integrated PL intensity quickly decreased when thickness of distortion quantum well was 20 nm or more, while in case of quantum wire, integrated PL intensity did not decrease up to the height of 40 nm at the tip. These results suggest that high quality quantum wire with fewer damage can be easily obtained and that critical film thickness can be increased. (Example 4)

A sample was prepared by the same procedure as in Example 3 except that the composition of the cladding layer

5 inside the V-groove was $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$, and PL intensity was examined at 77 K. As a result, distinct light emission peaks from $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$ distortion quantum wire (40 nm in width; 18 nm in height) were found as shown in Fig. 7, and light emission intensity increased compared with that of the sample in Example 4. This may be attributable to the fact that the carriers in the V-groove could not go out of the V-groove and were concentrated on the active layer at the bottom of the V-groove because energy barrier is present on side walls of the V-groove. These results reveal that it is advantageous when preparing a laser element and the like.

(Example 5)

First, on an n-type (100) GaAs substrate 1, an n-type GaAs buffer layer 2 (0.5 μm), an n-type $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ cladding layer 3 (3 μm), an undoped $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ high resistance cladding layer 9 (1 μm), and an undoped GaAs cap layer (0.1 μm) were formed by MOCVD method in this order. On the surface of this epitaxial substrate, silicon nitride film was formed by PCVD method, and the surface was masked by photolithography method in such manner that the silicon nitride film 8 of 2 μm in width extending in [011] direction was aligned at every 2 μm . The masked sample was set again on the MOCVD system. After setting, temperature was raised to 700°C under arsine (AsH_3) atmosphere, and etching was performed using HCl gas, and a V-groove of 1.4 μm in depth having the {111} B faces 6 on both sides was formed. Immediately after etching was

097848 03004
F00220 B0458260

5
10
15
20
25

stopped, trimethyl gallium (TMG) was supplied with the temperature maintained at 700°C, and a GaAs quantum wire active layer 4 of 15 nm in height and 28 nm in lateral width was formed in the V-groove. Further, trimethyl aluminum (TMA) was supplied simultaneously with TMG, and a p-type $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ optical guiding layer 10 of 50 nm and a p-type $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ cladding layer 5 of 1 μm were prepared. Next, the supply of TMA was stopped, and a p-type GaAs contact layer 11 of 0.1 μm was formed. In this case, epitaxial growth was difficult to perform on the (111) B face 6, and no growth occurred on the side walls of the V-groove. As a result, GaAs quantum wire was formed self-matchingly at the bottom of the V-groove. By supplying HCl at a rate of about 1 sccm, i.e. by the same number of mols as III raw material even during the growth, deposition of AlGaAs polycrystal on the silicon nitride layer was prevented. This method to supply HCl during growth is preferably used in case aluminum composition of the GaAlAs layer is 0.4 or more. This enables selective growth of AlGaAs having high aluminum composition, and this is effective for confinement of carriers to the quantum wire active layer 4.

Electrodes are provided above and under the sample thus grown, and a laser element is prepared by cleaving to laser tips. Then, laser oscillation is obtained at a threshold as low as 1 mA.

In the above example, an active layer comprising a single quantum wire was used, whereas an active layer comprising a plurality of quantum wires may be used,

sandwiching such a thin film barrier layer that quantum wires can be optically coupled.

(Example 6)

First, on an n-type (100) GaAs substrate 1, an n-type GaAs buffer layer 2 (0.5 μm), an n-type $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ cladding layer 3 (2 μm), an n-type $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ optical guiding layer 13 (0.5 μm), an undoped $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ high resistance cladding layer 9 (1 μm) and an undoped GaAs cap layer 7 (0.1 μm) were formed by MOCVD method in this order. On the surface of this epitaxial substrate, silicon nitride film was formed by PCVD method, and the surface was masked by photolithography method in such manner that the silicon nitride film 8 of 2 μm in width extending in [011] direction was aligned at every 2 μm . The masked sample was set again on the MOCVD system. After the setting, temperature was raised to 700°C under arsine (AsH_3) atmosphere, and the etching was performed using HCl gas, and a V-groove of 1.4 μm in depth having the {111} B faces on both sides was formed. Immediately after the etching was stopped, trimethyl gallium (TMG) was supplied while maintaining the temperature at 700°C, and a GaAs active layer 4 of 15 nm in height and 28 nm in width was formed in the V-groove. Further, trimethyl aluminum (TMA) was supplied simultaneously with TMG, and a p-type $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ optical guiding layer 10 of 0.3 μm and a p-type $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ cladding layer 5 of 1 μm were prepared. Then, the supply of TMA was stopped, and a p-type GaAs cap layer 7 of 0.1 μm was prepared. In this case, it was difficult

laser of high quality and having light output suitable for practical application. Also, it is possible according to the present invention to easily obtain quantum wire having good quality distortion.

09785428-022004

5

10

15

20

25